Supporting Information for:
Conversion of Fe-NH_2 to Fe-N_2 with release of NH_3

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General Considerations

Unless otherwise noted, all compounds were prepared by literature procedures or purchased from commercial sources. All manipulations were carried out under a dinitrogen atmosphere by utilizing standard glovebox or schlenk techniques. Solvents were dried and deoxygenated by an argon sparge followed by passage through an activated alumina column purchased from S.G. Waters Company. All non-halogenated solvents were tested with a standard sodium-benzophenone ketyl solution to ensure the absence of oxygen and water.

NMR

NMR measurements were obtained on Varian 300, 400, or 500 MHz spectrometers. Deuterated solvents for these measurements were obtained from Cambridge Isotope Laboratories and were dried and degassed prior to use. All ^{1}H spectra were referenced to residual solvent peaks and all ^{31}P spectra were referenced to an external H_3PO_4 standard.

EPR

EPR X-band spectra were obtained on a Bruker EMX spectrometer with the aid of Bruker Win-EPR software suite version 3.0. The spectrometer was equipped with a rectangular cavity which operated in the TE_{102} mode. Temperature control was achieved with the use of an Oxford continuous-flow helium cryostat (temperature range 3.6 – 300 K). All spectra were recorded at 9.37 GHz with a microwave power of 20 mW, a modulation amplitude of 4 G, and a modulation frequency of 100 kHz.

X-Ray Crystallography

Data was obtained at low temperatures on a Siemens or Bruker Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.71073), performing φ-and ω-scans. Data for complex **4** was collected on with synchrotron radiation at the Stanford Synchrotron Radiation Laboratory (SSRL) beam line 12-2 at 17 keV using a single phi axis and recorded on a Dectris Pilatus 6M. The images were processed using XDS[1] and further workup of the data was analogous to the other datasets. All structures were solved by standard direct or Patterson methods and refined against F^2 using the SHELX program package.[2,3,4] All atoms, with the exception of hydrogens, have been anisotropically refined. The hydrogen atoms bonded to atoms of interest, namely N or O, have been located in the difference map and refined semi-freely. All other hydrogen atoms were included via a standard riding model.

In the structure of complex **1** a minor component of (TPB)FeCl was found in the difference map and modeled as disorder. Additional disorder of the BAr^F_4 counterion was found in complex **4**. This disorder was modeled as a rotational disorder of the CF_3 groups on one of the phenyl rings, but some of the resulting F ellipsoids still display significantly prolate shapes. We

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[1] W. Kabsch, *J. Appl. Cryst.* **1993**, *26*, 795.

[2] Sheldrick, G. M. *Acta Cryst.* **1990**, *A46*, 467.

[3] Sheldrick, G. M. *Acta Cryst.* **2004**, *A64*, 112.

[4] Müller, P. *Crystallography Reviews* **2009**, *15*, 57.

feel that the shape of these ellipsoids accurately describes the actual electron density due to the rotational disorder.

Magnetic Measurements.

Data was obtained using a Quantum Designs SQUID magnetometer running MPMSR2 software (Magnetic Property Measurement System Revision 2) at a field strength of 50000 G. Complexes were massed and then suspended in eicosane wax. Samples were then inserted into the magnetometer in plastic straws sealed under nitrogen with gelatin capsules. Loaded samples were centered within the magnetometer using the DC centering scan at 35 K. Data were acquired at 20-30 K (one data point every 2 K), and 30-300 K (one data point every 10 K). The magnetic susceptibility was adjusted for diamagnetic contributions using the constitutive corrections of Pascal's constants as well as a diamagnetic correction for the eicosane and capsule. Data workup, including simulations, was performed in the JulX software package.[5] Complex **5** displayed a lower than expected magnetic moment. NMR analysis of the sample indicated the presence of ~15% 12-crown-4, present as a result of the protocol for generation of the complex, where it is used to aid for removal of $NaBAr^F_4$. Accounting for this impurity leads to a magnetic moment consistent with the other samples.

Computational Methods

Geometry optimizations were performed using the Gaussian03 package.[6] The B3LYP exchange-correlation functional was employed with a 6-31G(d) basis set. The GDIIS algorithm was used. A full frequency calculation was performed on each structure to establish true minima. A model for the initial geometry of complex **2** used the crystallographically determined coordinates as a starting point for subsequent minimization. Atoms were then stripped away from this structure to reveal a $Fe(PMe_2Ph)_3^+$ as the starting point to determine the theoretical structure of $Fe(PMe_2Ph)_3^+$ by another minimization. Structural models and orbital/spin density pictures were generated from Gaussview 03.

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[5] http://ewww.mpi-muelheim.mpg.de/bac/logins/bill/julX_en.php

[6] Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

Synthesis of (TPB)FeMe , 1

(TPB)FeBr (0.400 g, 0.55 mmol) was dissolved in 15 mL of ether and cooled to -35° C. To this stirred solution was added a 1.6 M solution of MeLi in ether (0.620 mL, 0.99 mmol). After addition the solution was allowed to warm to room temperature and was stirred for an additional hour over which time the solution changed in color from a dark brown to a deep orange red. After this time, volatiles were removed and the remaining solids were extracted with 3 mL of benzene three times. Lyophilization of benzene resulted in a dark orange powder which was washed with 5 mL of cold pentane to yield (TPB)FeMe (0.352 g, 97%). X-ray quality crystals were grown from slow evaporation of a concentrated pentane solution of **1**. ^{1}H NMR (C_6D_6, δ): 74.48 (br s), 33.25 (s), 22.52 (s), 9.31 (br s), 5.73 (s), 2.65 (s), -2.33 (br s), -2.80 (s), -7.49 (br s), -16.33 (s). UV-Vis (THF) λ_{max}, nm (ε, M^{-1} cm^{-1}): 840 (120). Anal. Calc. for $C_{37}H_{57}BFeP_3$: C 67.19; H 8.69. Found: C 67.26; H 8.59. Solution magnetic moment (C_6D_6): 3.9 μ_B.

Synthesis of [(TPB)Fe][BAr^F$_4$] 2

A dark orange solution of **1** (0.037 g, 0.06 mmol) in 5 mL of Et_2O was cooled to -35° C. Once cooled, the solution was stirred while a similarly cooled solution of $HBAr^F{}_4 \cdot 2\ Et_2O$[7] in 5 mL of Et_2O was added dropwise over 5 min. After the addition, the solution was stirred at room temperature for an additional hour before being concentrated down to 1 mL. This solution was layered with 1 mL of pentane and cooled to -35° C for 2 days upon which time dark orange crystals of [(TPB)Fe][$BAr^F{}_4$] had formed (0.082 g, 97%). ^{1}H NMR (C_6D_6/THF-*d*$_8$, δ): 32.15 (br s), 25.78 (s), 23.99 (br s), 8.93 (br s), 8.27 (s, $BAr^F{}_4$), 4.55 (br s), 1.84 (br s), -1.24 (br s), -28.05 (s). UV-Vis (Et_2O) λ_{max}, nm (ε, M^{-1} cm^{-1}): 475 (1700), 765 (800). Anal. Calc. for $C_{68}H_{66}B_2F_{24}FeP_3$: C 54.10; H 4.41. Found: C 53.93; H 4.53.

Synthesis of [(TPB)Fe(N_2H_4)][BAr^F$_4$], 3

2 (0.356 g, 0.24 mmol) was dissolved in 10 mL in Et_2O and stirred. To this was added N_2H_4 (0.076 mL, 2.36 mmol) in one portion. Upon addition, the solution lightened slightly in color to a brown-orange. The solution was allowed to stir for 15 min before the solution was concentrated to 5 mL and layered with 5 mL of pentane. After 2 days at -35° C, dark orange crystals of [(TPB)Fe(N_2H_4)][$BAr^F{}_4$] had formed (0.324 g, 89%). ^{1}H NMR (C_6D_6/THF- *d*$_8$, δ): 53.72 (br s), 28.26 (s), 25.32 (s), 20.18 (br s), 8.28 (s, $BAr^F{}_4$) 7.67 (s, $BAr^F{}_4$), 8.14 (br s), 7.96 (br s), 3.00 (br s), 2.67 (br s), 0.30 (br s), -26.06 (s). UV-Vis (THF) λ_{max}, nm (ε, M^{-1} cm^{-1}): 800 (140). Anal. Calc. for $C_{68}H_{70}B_2F_{24}FeN_2P_3$: C 52.98; H 4.58; N 1.82. Found: C 53.03; H 4.63; N 1.70. Solution magnetic moment (THF-d^8): 3.46 μ_B.

Synthesis of [(TPB)Fe(NH_3)][BAr^F$_4$], 4

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[7] Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920-3922.

A solution of **3** (0.308 g, 0.20 mmol) in 10 mL of 1:6 THF:Benzene was rapidly stirred at RT for 12 h. After this time, the volatiles were removed in vacuo and the residue was taken up in Et_2O, filtered, and layered with pentane before being cooled to -35°. After 2 days, dark orange-red crystals of $[(TPB)Fe(NH_3)][BAr^F_4]$ had formed (0.264 g, 87%). ^1H NMR (C_6D_6/THF-d^8, δ): 68.22 (br s), 28.55 (s), 24.28 (s), 17.81 (br s), 8.34 (s, BAr^F_4), 7.68 (s, BAr^F_4), 5.74 (br s), 3.53 (s), 2.15 (br s), 1.22 (br s), -25.48 (s). UV-Vis (THF) λ_{max}, nm (ε, M^{-1} cm^{-1}): 871 (50). IR (KBr, cm-1): 3381 (ν[NH]) Anal. Calc. for $C_{68}H_{69}B_2F_{24}FeNP_3$: C 54.24; H 4.55; N 0.92. Found: C 53.47; H 4.72; N 0.94. Solution magnetic moment (THF- d_8): 3.63 μ_B.

Synthesis of (TPB)FeNH$_2$, 5

A solution of **2** (0.300 g, 0.20 mmol) in 5 mL of Et_2O was stirred over powdered $NaNH_2$ (0.077 g, 1.99 mmol) for 1.5 h at room temperature. Over this time, the solution darkened from orange to a dark brown. Volatiles were removed and the remaining residue was extracted with 40 mL of pentane to yield a pale orange solution. To this solution was added 12-crown-4 (0.070 g, 0.40 mmol) to aid in the removal of $NaBAr^F_4$, and solids began to precipitate. The solution was allowed to stand for 1 h before filtration. Removal of solvent for 3 h at 70° C resulted in $(TPB)FeNH_2$ as a dark orange powder (0.060 g, 0.09 mmol, 46%). Crystals suitable for X-ray diffraction were grown from slow evaporation of a concentrated ethereal solution. Due to the presence of a small amount of 12-crown-4 that had similar solubility properties to the product, satisfactory combustion analysis was not obtained for **5**. ^1H NMR (C_6D_6, δ): 91.12 (br s), 38.21 (s), 25.42 (s), 4.12 (br s), 1.55 (br s), 0.21 (br s), -3.04 (br s), -5.93 (br s), -20.19(s). UV-Vis (THF) λ_{max}, nm (ε, M^{-1} cm^{-1}): 700 (90), 930 (80). Solution magnetic moment (C_6D_6): 4.05 μ_B. We also wish to note that trace amounts (<3%) of the neutral complex $(TPB)Fe(N_2)$ are typically detected by NMR spectroscopy in preparations of **5**. $(TPB)Fe(N_2)$ and **5** also have similar solubility properties.

Synthesis of (TPB)FeOH, 6

2 (0.80 g, 0.05 mmol) was dissolved in 5 mL of Et_2O and stirred over NaOH (0.063 g, 1.6 mmol) at room temperature for 2 h during which the color of the solution darkened to a deep brown. Volatiles were removed from the solution and the resulting solids were extracted with pentane to yield Synthesis of (TPB)FeOH (0.027, 77%) as a brown powder. Crystals suitable for X-Ray diffraction were grown by a slow evaporation of a concentrated Et_2O solution. ^1H NMR (C_6D_6, δ): 89.55 (br s), 39.07 (s), 24.70 (s), 6.71 (s), 4.08 (s), 1.55 (br s), -0.52 (br s), -6.00 (br s), -21.02 (s). UV-Vis (THF) λ_{max}, nm (ε, M^{-1} cm^{-1}): 870 (230), 700 (218). Anal. Calc. for $C_{36}H_{55}BFeOP_3$: C 65.18; H 8.36; N 0. Found: C 65.15; H 8.28; N none found. Solution magnetic moment (C_6D_6): 4.12 μ_B.

Protonation of 5

A 20 mL scintillation vial was charged with **5** (0.005 g, 0.007 mmol) and $HBAr^F_4 \cdot 2Et_2O$ (0.008 g, 0.007 mmol) and cooled to -35° C. 2 mL of similarly cooled Et_2O was added to the mixture and the color of the solution lightened rapidly. The solution was allowed to warm to room temperature over 30 minutes before volatiles were removed to yield **4** (0.010 g, 0.006 mmol, 91%). The identity of the product was determined via ^{1}H NMR which was identical to that observed for **4**.

Reduction of 4

A 20 mL scintillation vial was charged with **4** (0.025 g, 0.016 mmol) and KC_8 (0.0024 g, 0.018 mmol). 2 mL of Et_2O were added and the resulting dark suspension was allowed to stir for 2 h at RT. After this time, the solution was filtered and volatiles were removed to yield (TPB)Fe(N_2) as a brown solid. The identity of the product was determined via ^{1}H NMR which was identical to the previously reported values for (TPB)Fe(N_2).

Monitored Conversion of 3 to 4

3 (0.020 g, 0.013 mmol) was dissolved in a 6:1 mixture of C_6D_6:THF-d_8. The resulting solution was transferred to an NMR tube equipped with a capillary containing a solution of (TPB)FeBr in a 6:1 mixture of C_6D_6:THF-d_8 as an internal standard. This NMR tube was sealed with a J-Young valve and was placed into a 500 MHz spectrometer which had been preheated to 60° C. The reaction was monitored via single scans every minute for 4 hours during which time complete and clean conversion from **3** to **4** was observed. After the reaction was complete, an aliquot of the headspace was analyzed by GC for the presence of H_2. After this, volatiles were vacuum transferred onto a solution of HCl in THF. After this, volatiles were removed and the resulting solids were diluted with water to appropriate volumes to test for the presence of NH_3 via the indophenol test,[8] or N_2H_4 with *p*-dimethylaminobenzaldehyde.[9] The relative amounts of products are compiled in Table 1 of this document.

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[8] Weatherburn, M.W. *Anal. Chem.* **1967**, *39*, 971-974.

[9] Watt, G. W.; Chrisp, J. D. *Anal. Chem.* **1952**, *24*, 2006-2008.

Figure 1. ^{1}H NMR Spectrum of (TPB)FeMe in C_6D_6 (**1**)

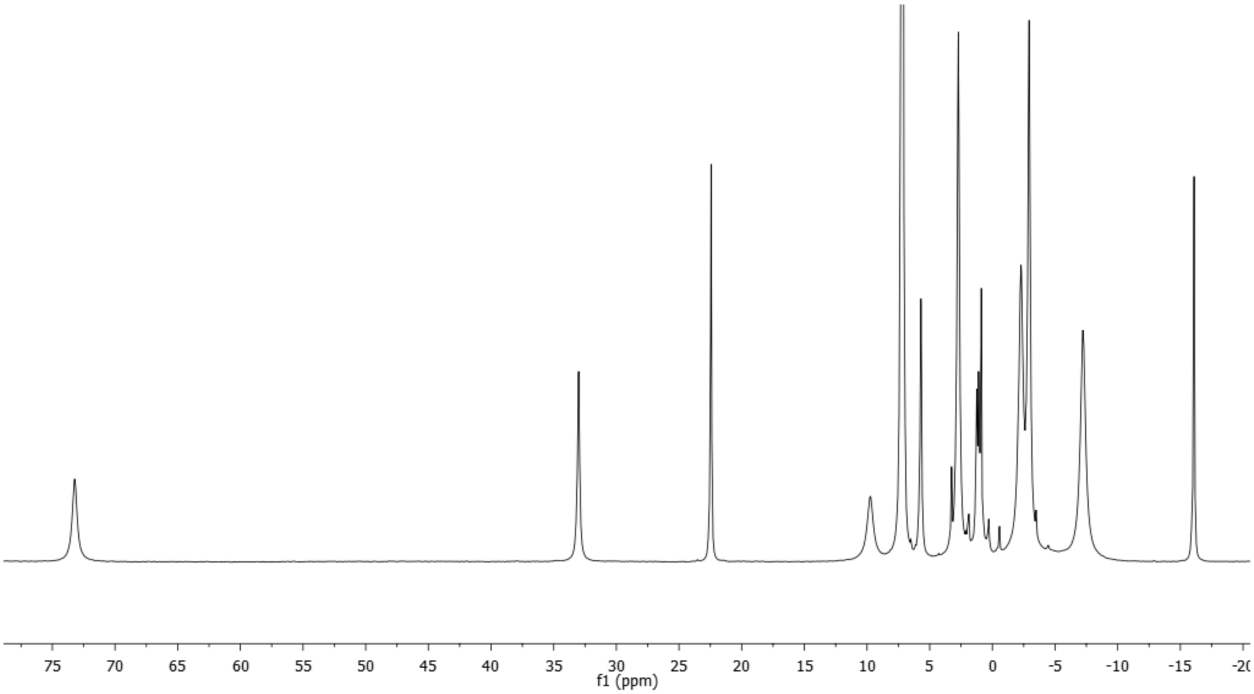


Figure 2. ^{1}H NMR Spectrum of [(TPB)Fe][BAr$^F_4$] in a 6:1 mixture of C_6D_6:THF-d_8 (**2**)

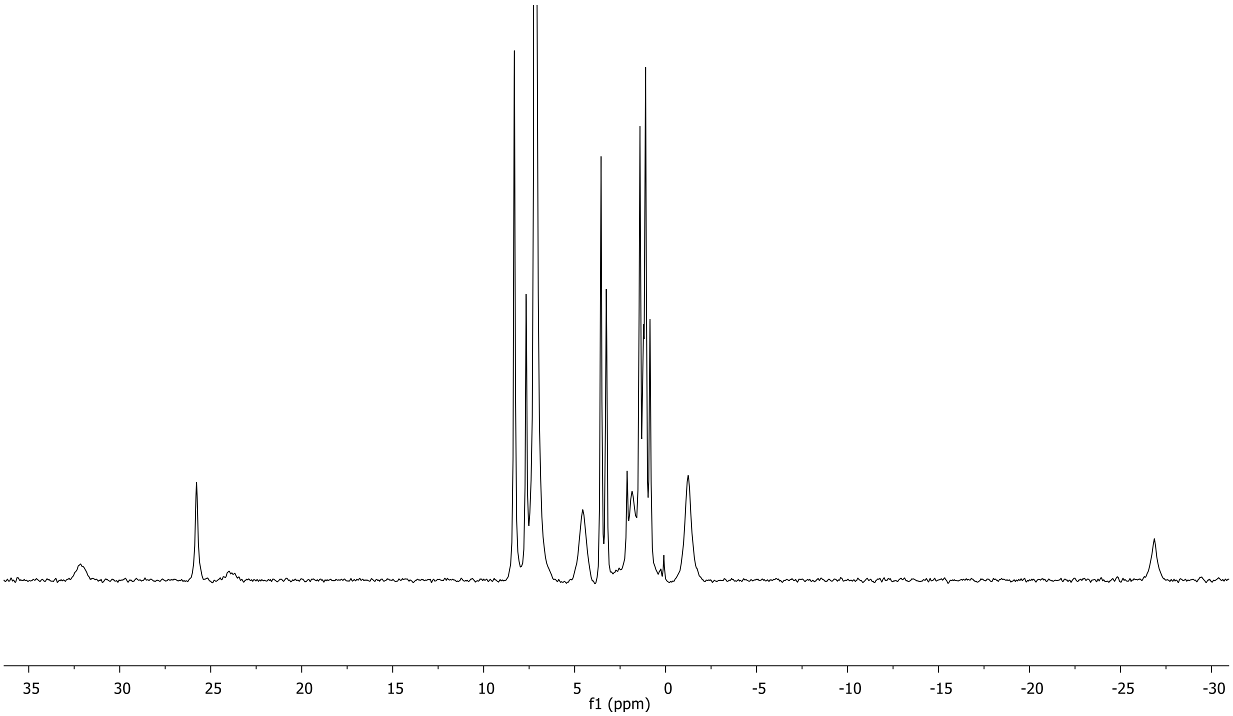


Figure 3. ^{1}H NMR Spectrum of $[(TPB)Fe(N_2H_4)][BAr^F_4]$ in a 6:1 mixture of C_6D_6:THF-*d_8* (**3**)

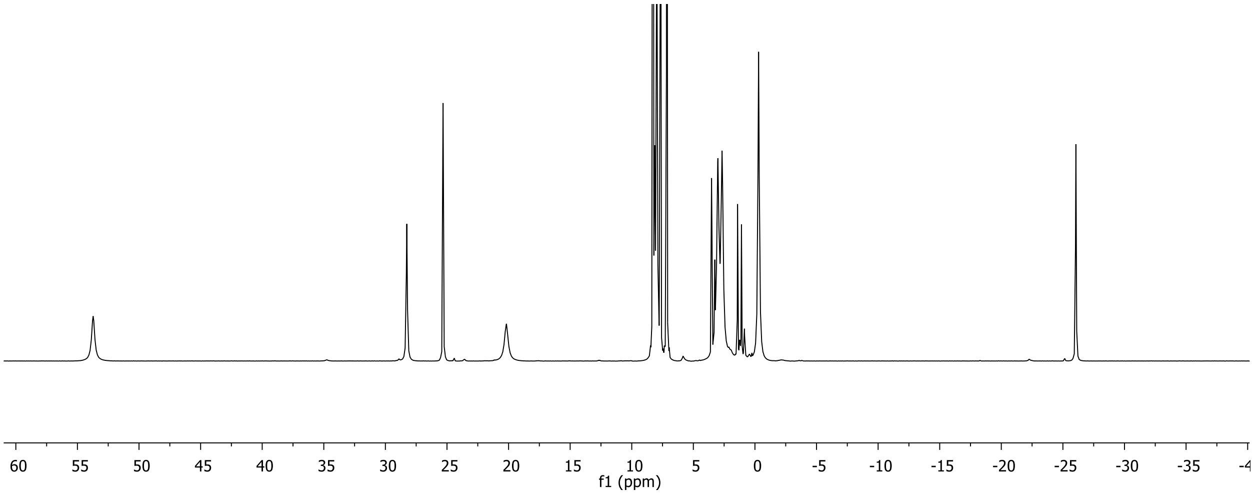


Figure 4. ^{1}H NMR Spectrum of $[(TPB)Fe(NH_3)][BAr^F_4]$ in a 6:1 mixture of C_6D_6:THF-*d_8* (**4**)

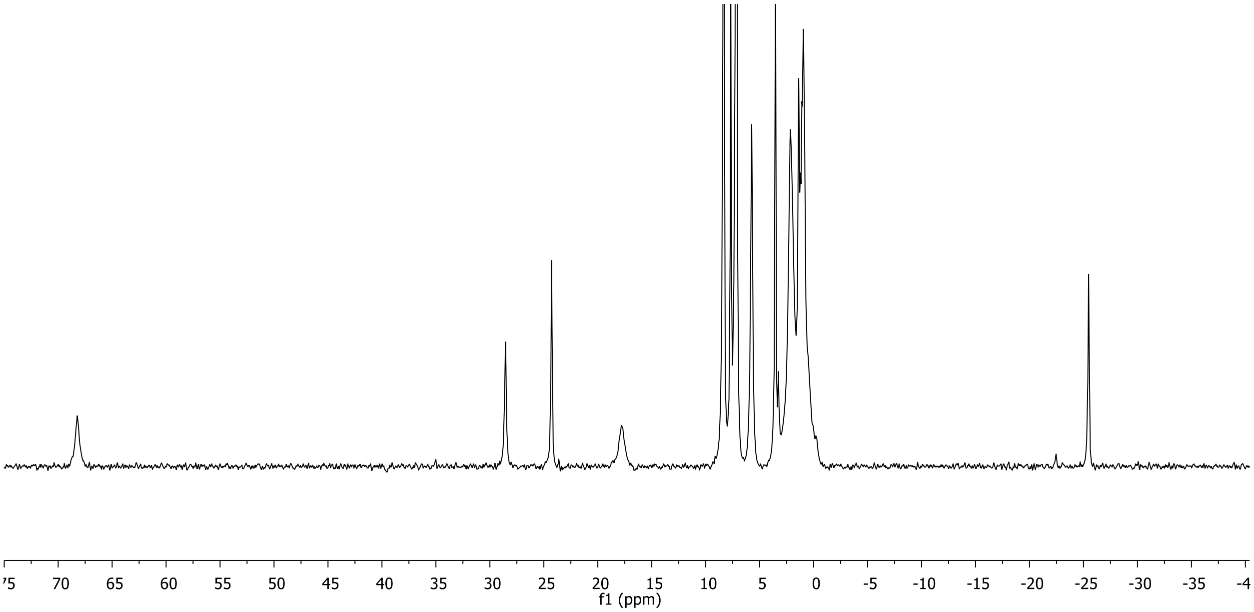


Figure 5. ^{1}H NMR Spectrum of (TPB)FeNH$_2$ in C$_6$D$_6$ (**5**)

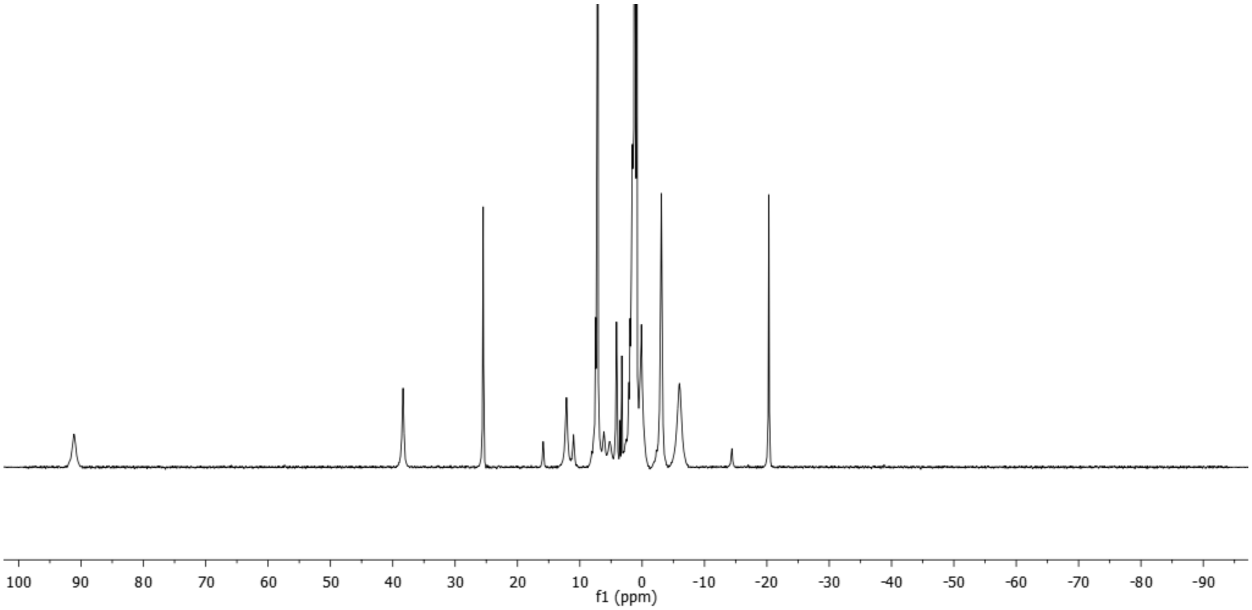


Figure 6. ^{1}H NMR Spectrum of (TPB)FeOH in C$_6$D$_6$ (**6**)

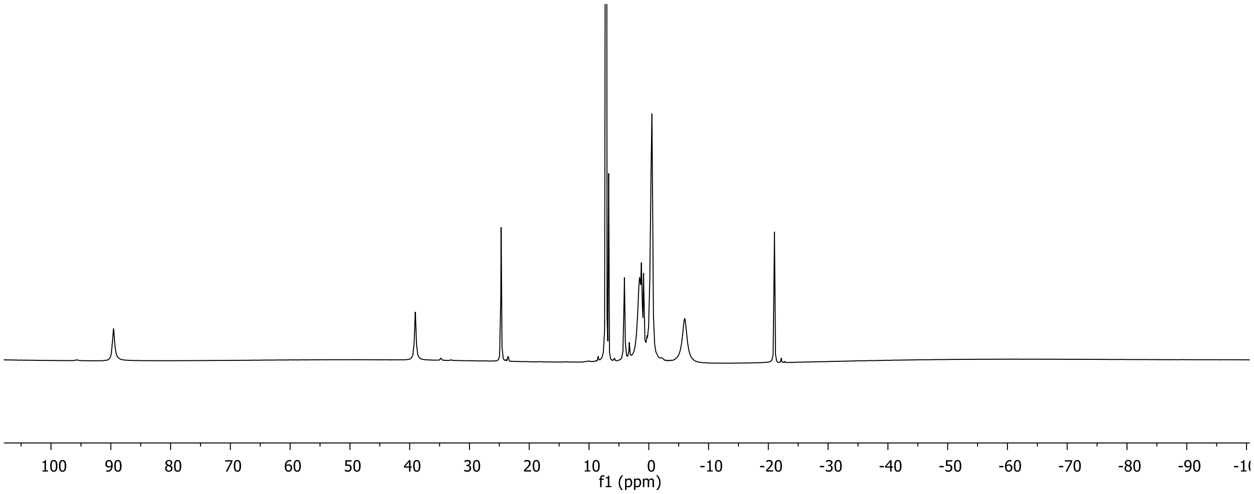


Figure 7. 8 K EPR Spectrum of (TPB)FeMe in Toluene (**1**)

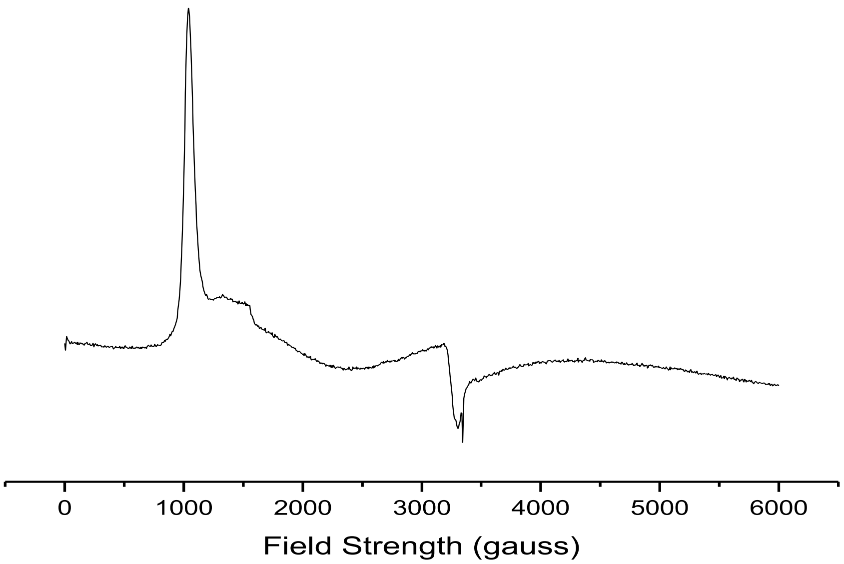


Figure 8. 10 K EPR Spectrum of [(TPB)Fe][BAr$^F{}_4$] in 2:1 Toluene:Et$_2$O (**2**)

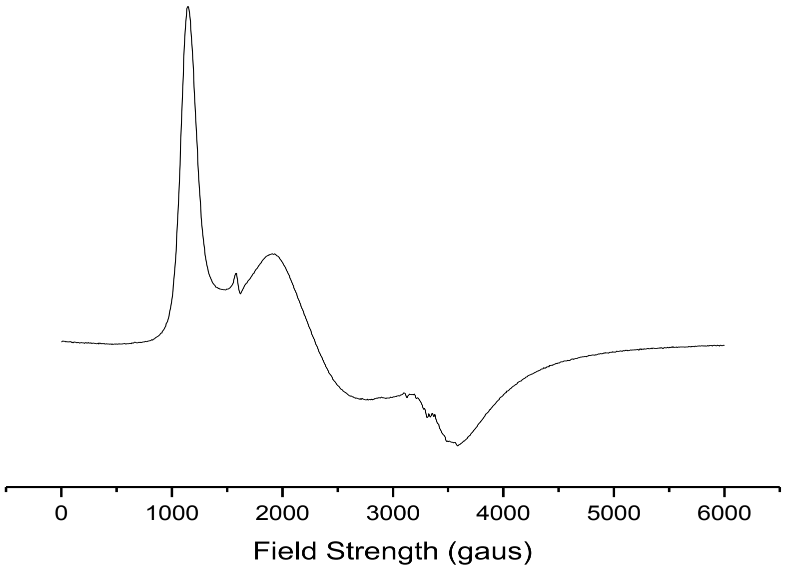


Figure 9. 10 K EPR Spectrum of $[(TPB)Fe(N_2H_4)][BAr^F_4]$ in 2-MeTHF (**3**)

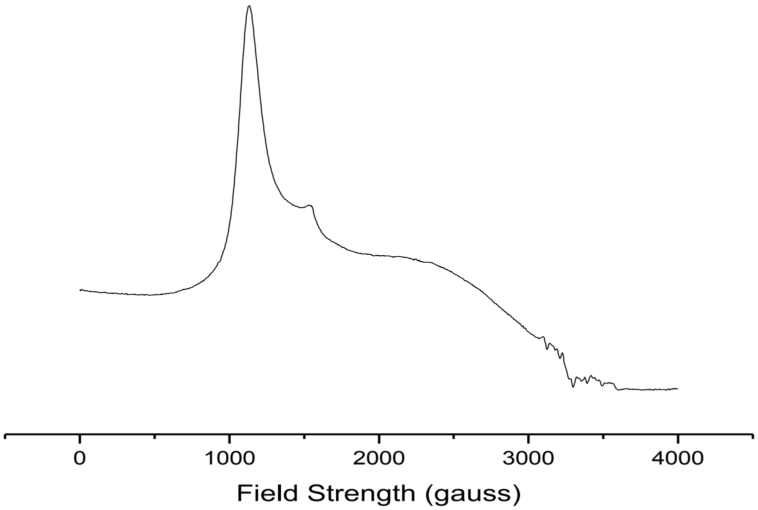


Figure 10. 10 K EPR Spectrum of $[(TPB)Fe(NH_3)][BAr^F_4]$ in 2-MeTHF (**4**)

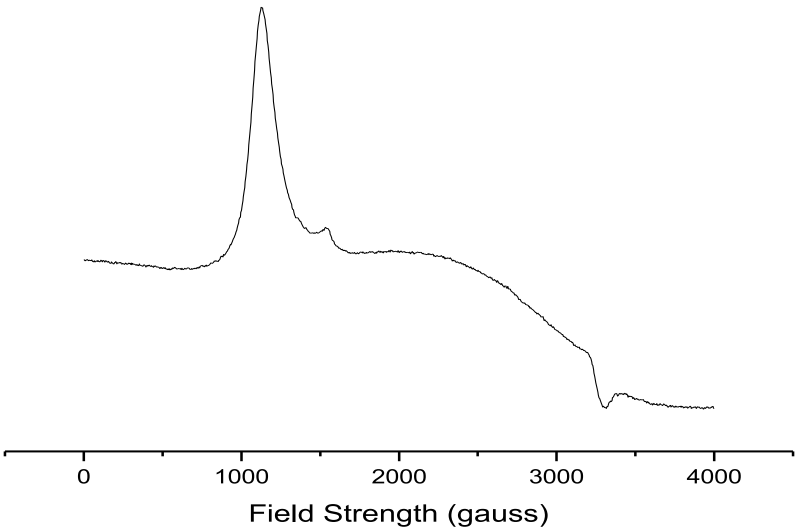


Figure 11. 10 K EPR Spectrum of (TPB)FeNH$_2$ in 2-MeTHF (**5**)

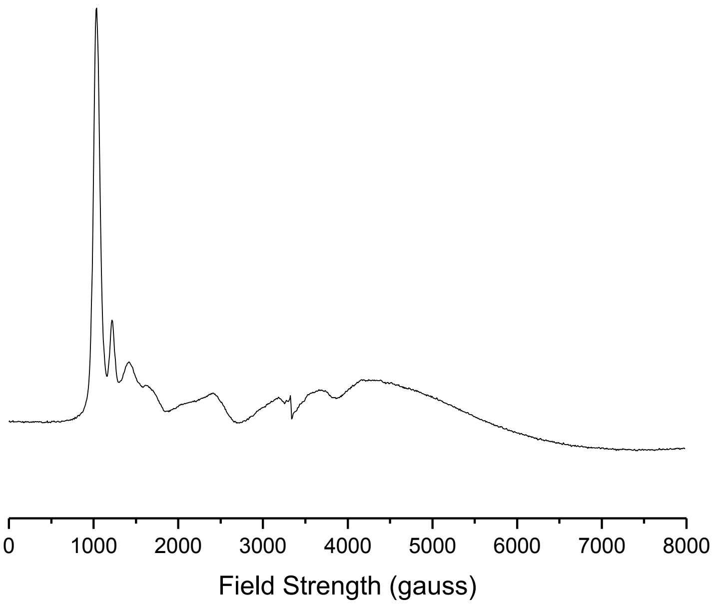


Figure 12. 10 K EPR Spectrum of (TPB)FeOH in Toluene (**6**)

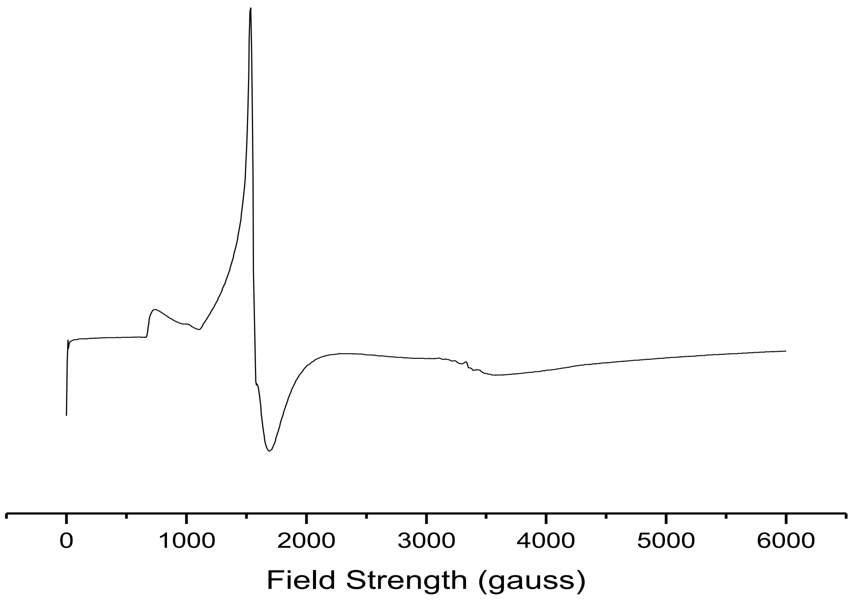


Figure 13. UV-Vis Spectrum of (TPB)FeMe in THF (**1**)

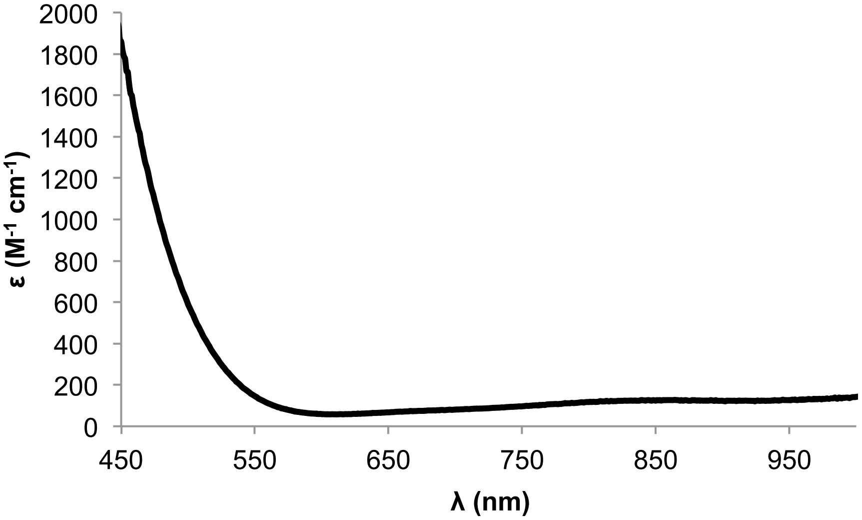


Figure 14. UV-Vis Spectrum of [(TPB)Fe][BAr$^F{}_4$] in Et$_2$O (**2**)

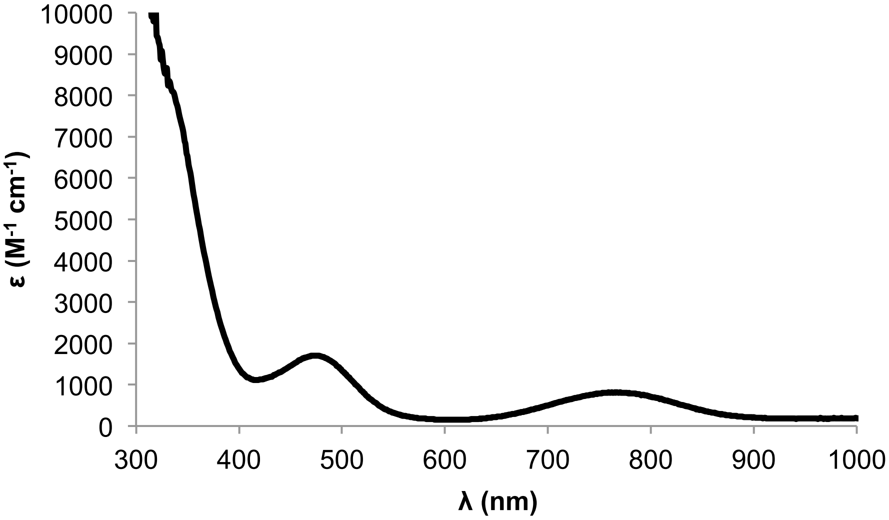


Figure 15. UV-vis Spectrum of [(TPB)Fe(N_2H_4)][BAr$^F_4$] in THF (**3**)

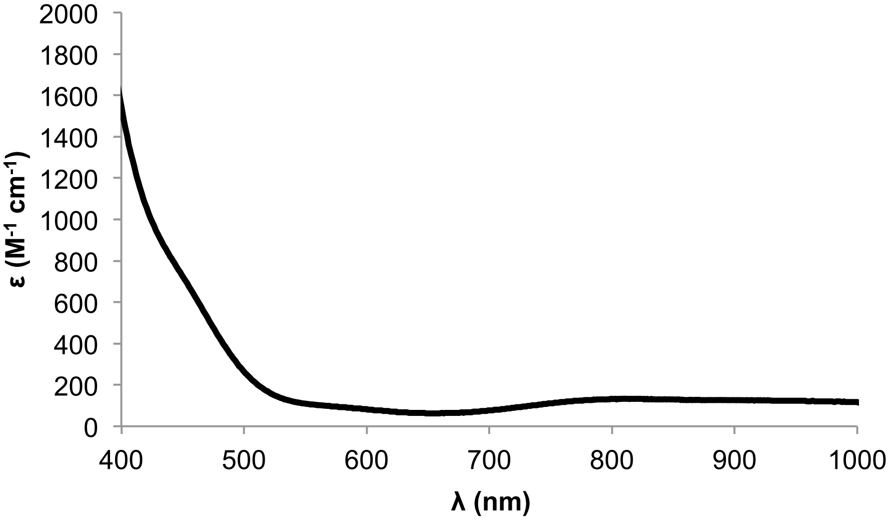


Figure 16. UV-vis Spectrum of [(TPB)Fe(NH_3)][BAr$^F_4$] in THF (**4**)

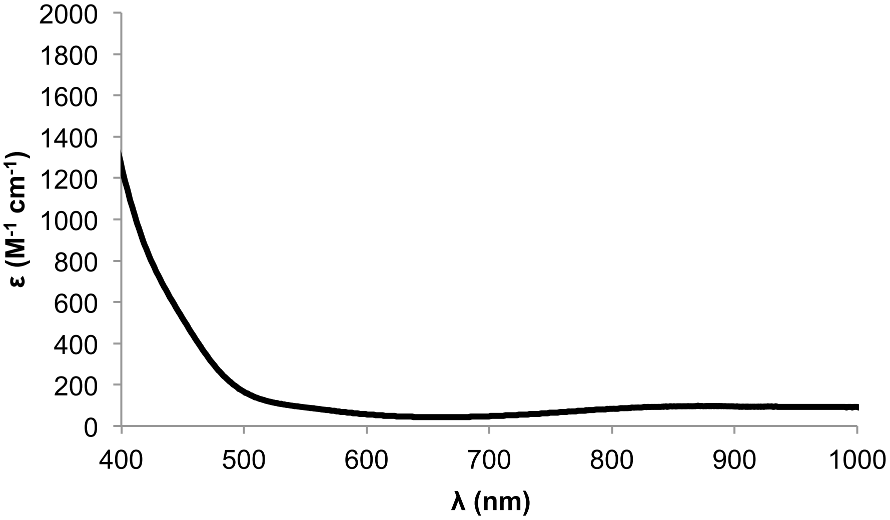


Figure 17. UV-vis Spectrum of (TPB)FeNH$_2$ in THF (**5**)

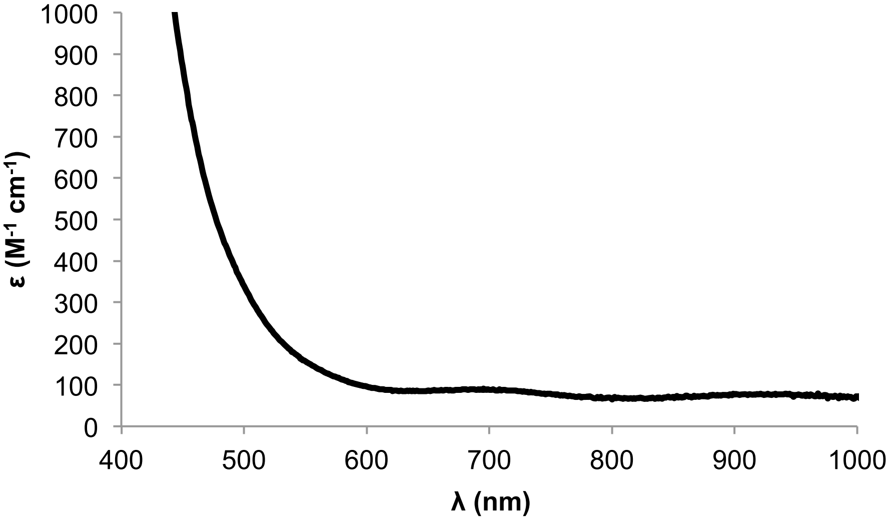


Figure 18. UV-Vis Spectrum of (TPB)FeOH in THF (**6**)

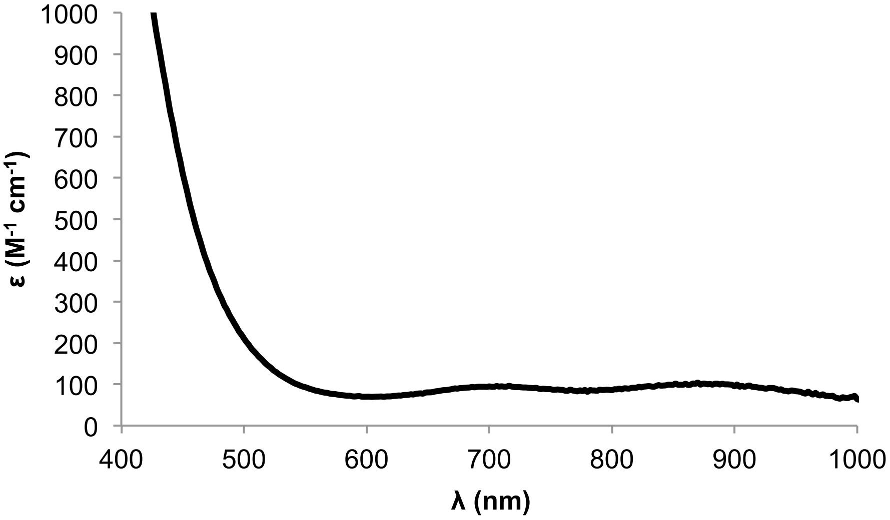


Figure 19. Titration of THF into a 4 mL ethereal solution of **2**

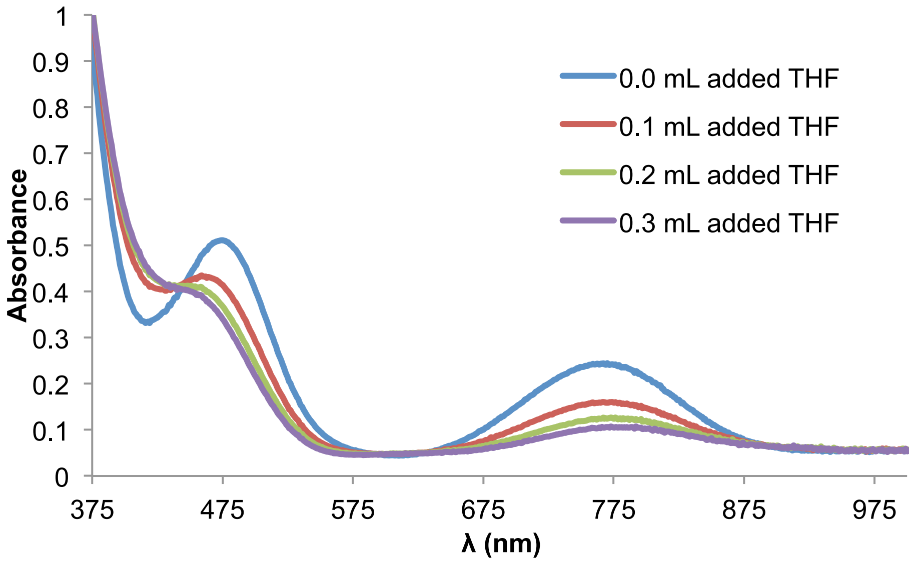
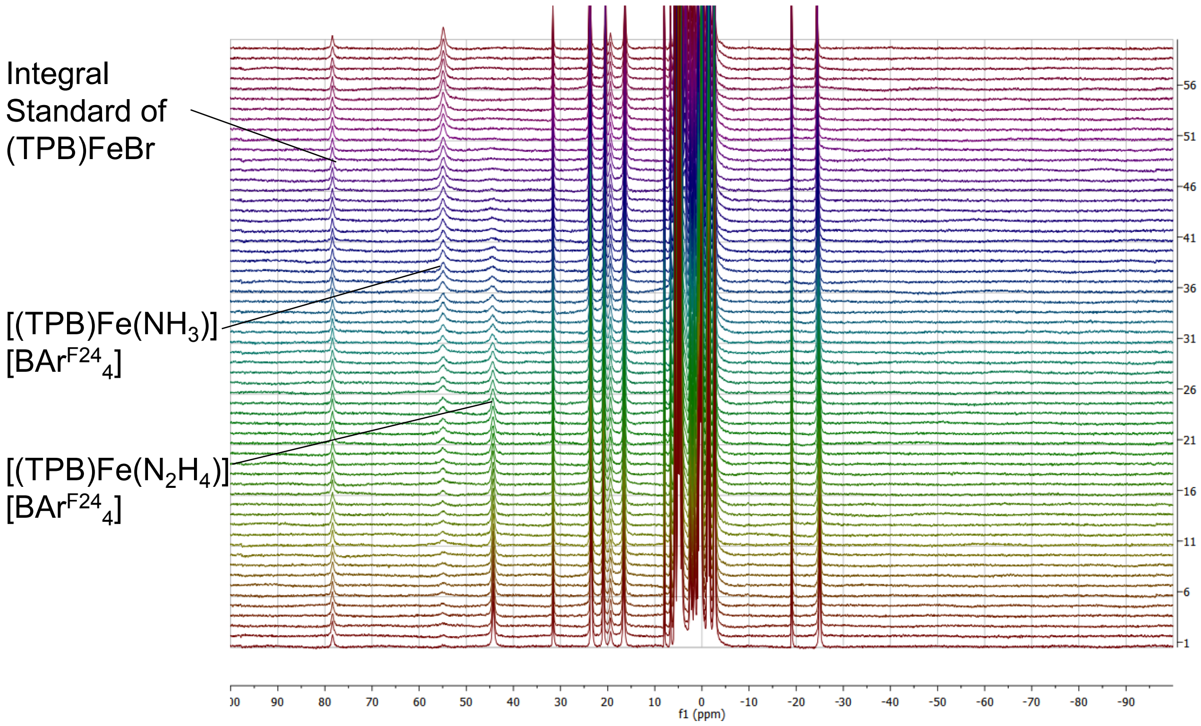


Figure 20. NMR traces of the monitored decomposition of **3** to **4**

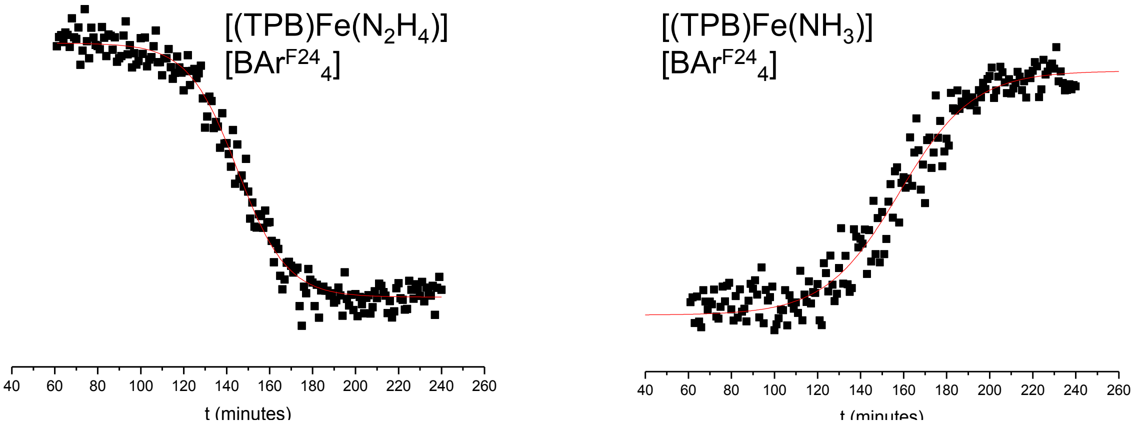

Integral Standard of (TPB)FeBr

$[(TPB)Fe(NH_3)][BAr^{F24}_4]$

$[(TPB)Fe(N_2H_4)][BAr^{F24}_4]$

Conditions: 0.037 M, C_6D_6/THF-d^8, 60 °C, Total time = 4h. Only 2nd hour is shown.

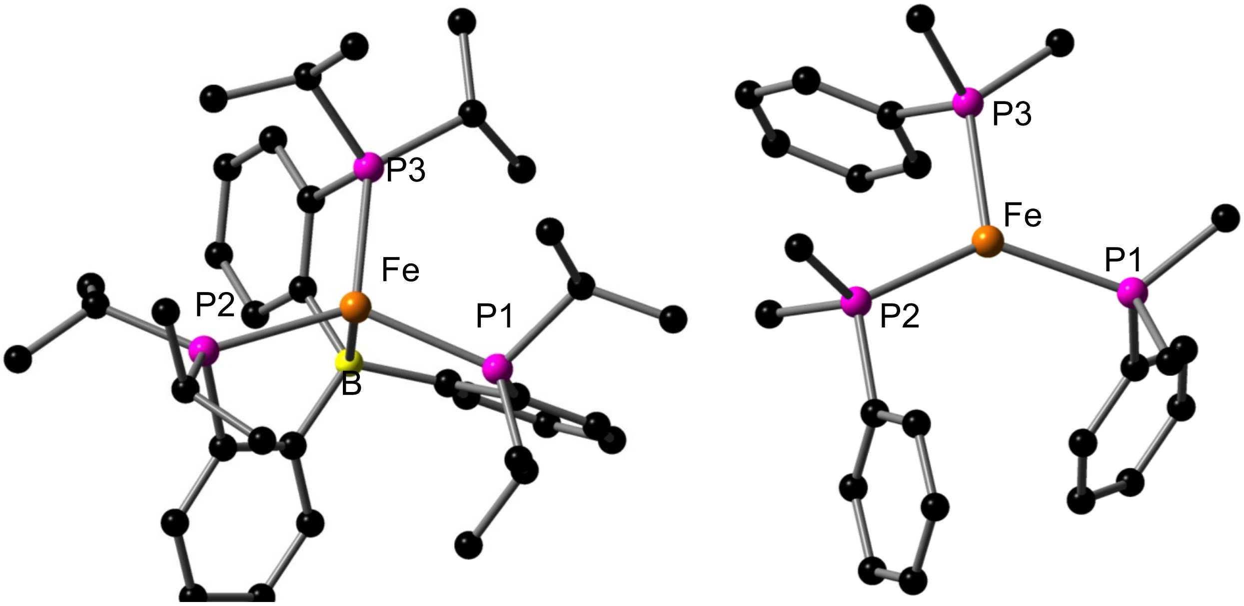
Figure 21. Kinetic plots of the monitored decomposition of **3** to **4**



Kinetic traces obtained from ^{1}H NMR integration. The red lines may serve as guides to the eye. No appreciably reaction occurred over the first 60 minutes of the reaction.

Figure 22. Geometries of [(TPB)Fe]$^+$ and [(Me$_2$PhP)$_3$Fe]$^+$ optimized

at the B3LYP/6-31G(d) level



Selected bond distances [Å] and angles [°]: $[(TPB)Fe]^+$: Fe–P1 2.426, Fe–P2 2.481, Fe–P3 2.460, Fe–B 2.189, P1–Fe–P2 137.5, P1–Fe–P3 109.1, P2–Fe–P3 113.2; $[(Me_2PhP)_3Fe]^+$: Fe–P1 2.359, Fe–P2 2.328, Fe–P3 2.350, P1–Fe–P2 134.8, P1–Fe–P3 113.1, P2–Fe–P3 111.7.

Optimized coordinates [Å] for [(TPB)Fe]$^+$:

Fe	0.00415000	-0.16241600	-0.77675900
P	-2.16349100	-1.24719000	-0.66738800
P	2.39121900	-0.83777200	-0.74771500
P	-0.31345400	2.27645200	-0.74537300
C	2.09021700	-1.73435800	0.82972400
C	4.02952400	1.02631900	0.64266200
H	3.98567100	0.45071500	1.57275400
H	3.19104000	1.72365500	0.64140500
H	4.95767100	1.60939200	0.65520800
C	-2.51735800	-0.85749000	1.09566800
C	-2.75787900	2.84164700	0.59302900
H	-2.24972100	3.20855200	1.49066600
H	-2.90111300	1.76680700	0.71127400
H	-3.74621500	3.31410800	0.55282800
C	0.96713000	-1.34366200	1.61726000
C	0.68267900	1.41376900	1.69824000
C	-3.77585900	-1.11913600	1.66212900
H	-4.53614800	-1.64204200	1.09100300
C	-1.50541500	-0.21277600	1.85301900
C	-1.85207300	0.20954700	3.15263700
H	-1.11562400	0.74145000	3.74897600
C	0.63534800	3.23145700	-2.06275600
H	0.57728600	4.28918000	-1.78194000
C	1.88147700	2.83955400	3.29296500
H	2.40769300	2.94283300	4.23815900
C	0.69310600	-2.13340400	2.75608400
H	-0.16599700	-1.88793000	3.37259400
C	4.03129200	0.10104900	-0.58072200
H	4.06604600	0.72216800	-1.48419000
C	1.38189800	1.59489600	2.90786900
H	1.54195100	0.73989400	3.56048800
B	0.03447200	-0.03107800	1.40854000
C	5.27977700	-0.79677000	-0.55921200
H	6.17024200	-0.16055800	-0.49330400
H	5.38965200	-1.41148800	-1.45674600
H	5.28761200	-1.45308000	0.31716600
C	1.72157800	3.94568000	2.45737900
H	2.12008100	4.91463800	2.74408600
C	1.05459100	3.79624400	1.24157800
H	0.95646000	4.65573100	0.58420600
C	2.77223500	-2.14130600	-2.05044100
H	3.66239200	-2.68641700	-1.71685100
C	-4.07155000	-0.72325700	2.96514500
H	-5.04800100	-0.93619400	3.39051300
C	-3.10700900	-0.04189100	3.70690700

H	-3.32936500	0.29181200	4.71691400
C	2.87573600	-2.83838200	1.19803000
H	3.71142600	-3.14386600	0.57548300
C	-1.96911100	3.20280400	-0.67407900
H	-2.51737400	2.81757600	-1.54509900
C	1.62859900	-3.14880400	-2.20719100
H	0.71343900	-2.65749200	-2.56047300
H	1.40294400	-3.66587600	-1.27050000
H	1.89809900	-3.90564800	-2.95299300
C	1.49436100	-3.21131000	3.13086000
H	1.25256900	-3.77768600	4.02619200
C	2.11687300	2.84858500	-2.14500700
H	2.24202800	1.80944900	-2.46700100
H	2.62947700	2.97816400	-1.18858400
H	2.61717700	3.48566700	-2.88385400
C	-2.49731300	-3.09116600	-0.81402900
H	-3.54555800	-3.21968300	-0.51323400
C	2.59216700	-3.56984800	2.34988300
H	3.21486600	-4.41610400	2.62556400
C	-1.61976400	-3.87498400	0.17378600
H	-1.85554000	-4.94310500	0.10319500
H	-1.78498100	-3.56065100	1.20749500
H	-0.55428900	-3.75363600	-0.04648600
C	0.53094900	2.55057600	0.86165400
C	-1.86943800	4.73224900	-0.80367000
H	-2.87736400	5.16043800	-0.75057800
H	-1.42999600	5.06125000	-1.74899100
H	-1.29175300	5.16729800	0.01900400
C	-2.95949200	-0.11225400	-3.13193300
H	-2.81329100	-1.04459900	-3.68700100
H	-2.00927500	0.43395300	-3.13573300
H	-3.68632300	0.48853300	-3.69112200
C	-3.47778300	-0.36144900	-1.70257400
H	-3.55367100	0.61070400	-1.20046300
C	-2.34128800	-3.61958100	-2.24860700
H	-1.32591600	-3.46834000	-2.62965700
H	-3.03896300	-3.15266000	-2.94927700
H	-2.53763200	-4.69785800	-2.26329900
C	-0.04759800	3.05060900	-3.43027100
H	-1.09647000	3.36299400	-3.42897900
H	-0.00706500	2.00371300	-3.75748600
C	3.08823800	-1.45897600	-3.39314100
H	3.31866300	-2.21769600	-4.14966000
H	3.94741000	-0.78399700	-3.33422400
H	2.22923900	-0.88166100	-3.75845100
C	-4.87834200	-0.99390800	-1.73157800

H	-5.54599600	-0.36236200	-2.32962300
H	-4.87513300	-1.98675200	-2.19255400
H	-5.32164500	-1.07767600	-0.73669900
H	0.47189800	3.64859800	-4.18772700

Optimized coordinates [Å] for $[(Me_2PhP)_3Fe]^+$:

Fe	0.15864700	-0.18495700	-0.99760500
P	-0.96396300	1.83613500	-1.46879900
P	-0.45971000	-2.22271000	-0.05600500
P	2.48332300	-0.04211700	-1.31271800
C	-2.26951200	-2.22907300	0.27519800
C	-1.24228800	2.66879600	0.14383800
C	-2.79182200	-2.06800000	1.56749900
C	4.03948300	-1.45884400	0.61288100
C	-0.64552100	3.89539800	0.47185600
H	-0.02266300	4.41711100	-0.24807900
C	-2.04536400	2.02460300	1.10222300
C	-2.25786700	2.60533100	2.35188400
H	-2.89062600	2.10308200	3.07801800
C	3.22714900	-1.29680000	-2.44619800
H	4.32141000	-1.26188800	-2.43248400
C	4.38348500	-0.67980900	2.87994900
H	4.81234400	-0.82007700	3.86773800
C	-4.17301300	-2.01522100	1.77110700
H	-4.56274900	-1.90088900	2.77861400
C	0.31804700	-2.68760000	1.54990900
H	1.38960600	-2.83560300	1.38660000
C	4.58567000	-1.63819900	1.88602900
H	5.17639900	-2.52519600	2.09670500
C	3.63159400	0.46273300	2.59776700
H	3.47437400	1.21562800	3.36480600
C	3.08377800	0.64390800	1.32807100
H	2.50486800	1.54243900	1.12392600
C	-0.21389600	-3.73662900	-1.09026300
H	-0.63896300	-4.62100300	-0.60524200
C	-0.85737200	4.47065600	1.72657200
H	-0.39598100	5.42490200	1.96403800
C	-1.66358000	3.82933600	2.66729400
H	-1.83040700	4.28140300	3.64050500
C	-3.16079100	-2.32427200	-0.80796000

H	-2.78261000	-2.44971700	-1.82004800
C	3.28247400	1.51522500	-1.91488900
H	2.90698900	1.75077900	-2.91604500
C	-5.04871600	-2.11906600	0.69010800
H	-6.12191000	-2.08279500	0.85179800
C	-2.66656800	1.64342000	-2.16885400
H	-3.18590300	2.60610400	-2.21168900
C	-4.53907500	-2.27482500	-0.60131300
H	-5.21468500	-2.36443900	-1.44718900
C	3.28537900	-0.31297600	0.31747500
C	-0.23933400	3.11974200	-2.57722600
H	0.77356200	3.37847300	-2.25945300
H	2.88637400	-1.08677000	-3.46523900
H	2.89836600	-2.30593900	-2.18218500
H	3.02794700	2.34344400	-1.24739500
H	4.37260400	1.42000600	-1.95477900
H	0.85730500	-3.89883800	-1.24746400
H	-0.68525200	-3.61298900	-2.06920800
H	-0.11632500	-3.60480000	1.96078100
H	0.20638200	-1.87762100	2.27591300
H	-0.85392700	4.02578200	-2.60403500
H	-0.18044400	2.70383300	-3.58796700
H	-3.25191000	0.95080000	-1.55774000
H	-2.59769400	1.23085800	-3.18107000
H	-2.51936000	1.07248800	0.87329200
H	4.21949800	-2.21267100	-0.14752200
H	-2.13022700	-1.99363600	2.42490400

Mulliken atomic spin densities for **2**

1	Fe	3.253912
2	P	-0.027171
3	P	-0.010617
4	P	-0.015937
5	C	-0.004907
6	C	0.000171
7	H	0.000020

8	H	0.000301
9	H	0.000144
10	C	-0.002614
11	C	0.000097
12	H	-0.000011
13	H	0.000408
14	H	-0.000066
15	C	0.031834
16	C	0.029533
17	C	0.003234
18	H	-0.000001
19	C	0.031179
20	C	-0.010984
21	H	0.000534
22	C	0.001306
23	H	0.000886
24	C	0.002732
25	H	-0.000716
26	C	-0.010913
27	H	0.000375
28	C	-0.001689
29	H	0.000232
30	C	-0.010241
31	H	0.000537
32	B	-0.267025
33	C	-0.000540
34	H	-0.000389

35	H	0.000017
36	H	0.000034
37	C	-0.004817
38	H	0.000268
39	C	0.002585
40	H	0.000043
41	C	0.007248
42	H	-0.000019
43	C	-0.006843
44	H	0.000321
45	C	0.003235
46	H	-0.000697
47	C	0.005544
48	H	-0.000087
49	C	-0.001772
50	H	0.000308
51	C	0.002233
52	H	-0.001672
53	H	-0.000551
54	H	0.000270
55	C	0.006515
56	H	-0.000827
57	C	-0.000211
58	H	0.000126
59	H	0.000133
60	H	-0.000055
61	C	0.009143

62	H	0.000978
63	C	-0.007547
64	H	0.000405
65	C	-0.000028
66	H	0.000024
67	H	-0.000020
68	H	-0.001178
69	C	-0.002002
70	C	0.000981
71	H	0.000333
72	H	-0.000026
73	H	-0.000056
74	C	0.001914
75	H	-0.000172
76	H	-0.000830
77	H	0.000312
78	C	-0.004719
79	H	0.000585
80	C	-0.000384
81	H	-0.000422
82	H	-0.000009
83	H	-0.000029
84	C	0.000389
85	H	-0.000118
86	H	-0.000747
87	C	-0.000078
88	H	0.000160

89	H	0.000030
90	H	-0.000011
91	C	-0.001228
92	H	-0.000593
93	H	0.000076
94	H	0.000043
95	H	-0.000115

Sum of Mulliken spin densities = 3.00000

Figure 23. MO and spin density diagram of [(TPB)Fe]$^+$ **2** optimized at the B3LYP/6-31G(d) level

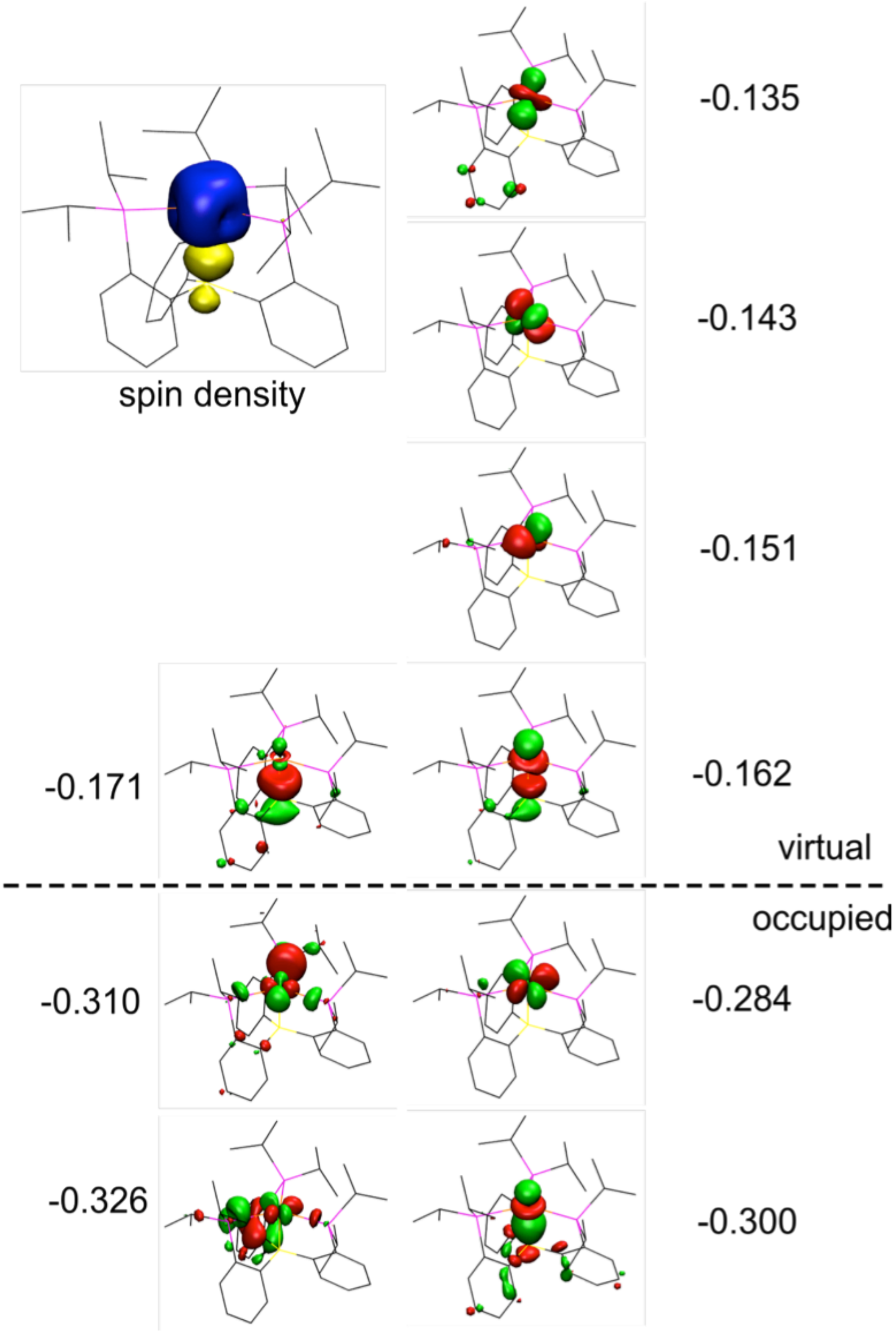


Figure 24. MO diagram offering a tentative explanation for the T-shaped distortion of **2**

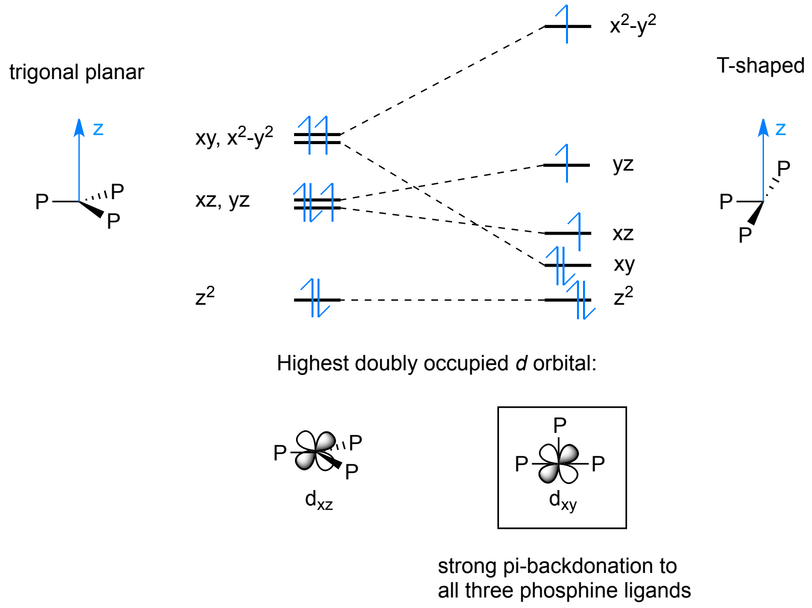
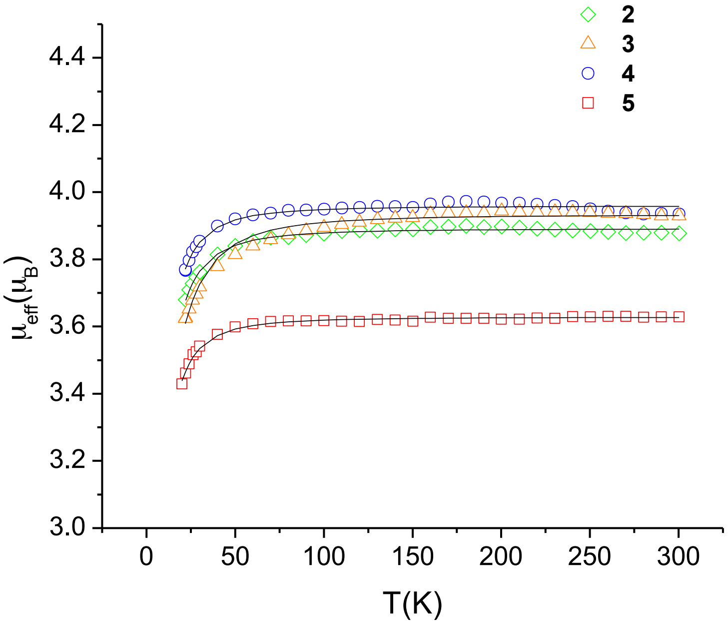
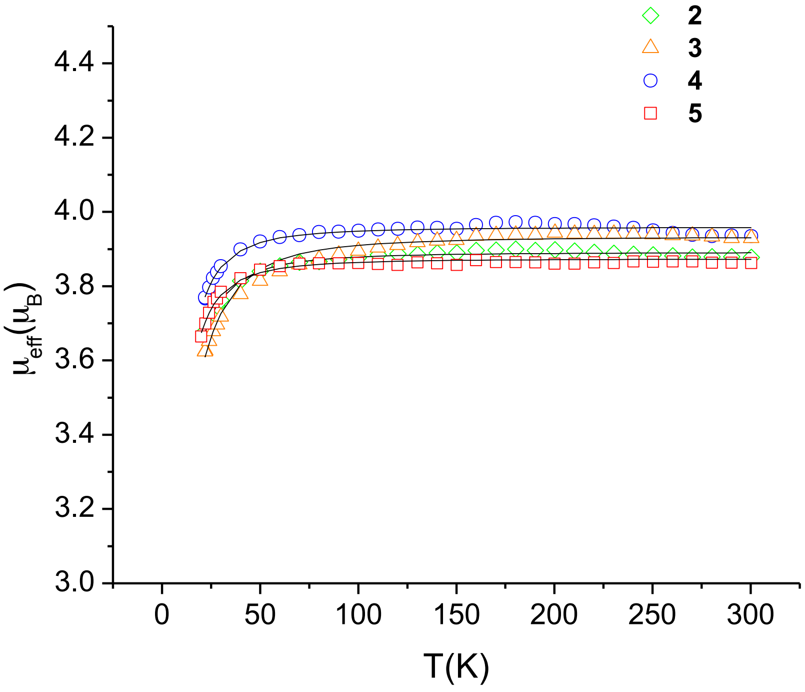


Figure 25. Variable Temperature Magnetic data for **2-5**



Data corrected for ~15% diamagnetic impurity of 12-crown-4, verified by ^{1}H NMR integration, in **5**



Simulation Parameters

Compound	S	g	D (cm^{-1})
$[TPB^{iPr}Fe][BAr^F_4]$	3/2	2.009	13.933
$[TPB^{iPr}Fe(N_2H_4)][BAr^F_4]$	3/2	2.031	19.937
$[TPB^{iPr}Fe(NH_3)][BAr^F_4]$	3/2	2.044	12.162
$(TPB^{iPr})Fe(NH_2)$	3/2	2.000	11.348

Table 1. Product quantification for the decomposition of **3** to **4**

Run	**Equiv H_2**	**Equiv N_2H_4**	**Equiv NH_3**
1	0.01	None det.	0.09
2	0.009	None det.	0.12
3	None det.	None det.	0.14

Table 2. Crystal data and structure refinement for (TPB)FeMe (**1**)

Identification code	jsa200m	
Empirical formula	C37 H57 B Cl Fe P3	
Formula weight	696.85	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.9554(3) Å	α= 91.4010(10)°.
	b = 11.5075(3) Å	β= 95.4060(10)°.
	c = 15.9312(4) Å	γ = 117.8130(10)°.
Volume	1763.16(8) $Å^3$	
Z	2	
Density (calculated)	1.313 Mg/m^3	
Absorption coefficient	0.665 mm^{-1}	
F(000)	744	
Crystal size	.456 x .304 x .209 mm^3	
Theta range for data collection	1.29 to 27.10°.	
Index ranges	-14<=h<=14, -14<=k<=14, -20<=l<=20	
Reflections collected	36496	
Independent reflections	7758 [R(int) = 0.0311]	
Completeness to theta = 27.10°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7758 / 338 / 402	
Goodness-of-fit on F^2	1.086	
Final R indices [I>2sigma(I)]	R1 = 0.0321, wR2 = 0.0813	
R indices (all data)	R1 = 0.0371, wR2 = 0.0860	
Largest diff. peak and hole	0.890 and -0.305 e.$Å^{-3}$	

Table 3. Crystal data and structure refinement for [(TPB)Fe][BAr$^F_4$] (**2**)

Identification code	mem130	
Empirical formula	C68 H66 B2 F24 Fe N0 P3 Si0	
Formula weight	1509.59	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 26.4056(9) Å	α= 90°.
	b = 19.7833(7) Å	β= 90°.
	c = 26.4402(9) Å	γ = 90°.
Volume	13812.1(8) Å^3	
Z	8	
Density (calculated)	1.452 Mg/m^3	
Absorption coefficient	0.393 mm^{-1}	
F(000)	6168	
Crystal size	0.32 x 0.30 x 0.26 mm^3	
Theta range for data collection	1.85 to 33.73°.	
Index ranges	-35<=h<=41, -30<=k<=30, -41<=l<=41	
Reflections collected	379408	
Independent reflections	27590 [R(int) = 0.0500]	
Completeness to theta = 33.73°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9046 and 0.8844	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	27590 / 18 / 951	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0496, wR2 = 0.1239	
R indices (all data)	R1 = 0.0744, wR2 = 0.1400	
Largest diff. peak and hole	0.740 and -0.532 e.Å^{-3}	

Table 4. Crystal data and structure refinement for $[(TPB)Fe(N_2H_4)][BAr^F_4]$ (**3**)

Identification code	jsa19_0m	
Empirical formula	C78 H68 B2 F24 Fe N2 P3	
Formula weight	1659.72	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 20.0031(7) Å	α= 90°.
	b = 25.7862(8) Å	β= 90°.
	c = 26.6970(8) Å	γ = 90°.
Volume	13770.4(8) Å^3	
Z	8	
Density (calculated)	1.601 Mg/m^3	
Absorption coefficient	0.404 mm^{-1}	
F(000)	6776	
Crystal size	0.46 x 0.26 x 0.15 mm^3	
Theta range for data collection	2.00 to 32.59°.	
Index ranges	-30<=h<=30, -39<=k<=39, -40<=l<=40	
Reflections collected	347031	
Independent reflections	25087 [R(int) = 0.0696]	
Completeness to theta = 32.59°	99.9 %	
Max. and min. transmission	0.9419 and 0.8361	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	25087 / 971 / 981	
Goodness-of-fit on F^2	0.937	
Final R indices [I>2sigma(I)]	R1 = 0.0531, wR2 = 0.1373	
R indices (all data)	R1 = 0.0872, wR2 = 0.1681	
Largest diff. peak and hole	1.295 and -0.755 e.Å^{-3}	

Table 5. Crystal data and structure refinement for $[(TPB)Fe(NH_3)][BAr^F_4]$ (**4**)

Identification code	xds_ascii	
Empirical formula	C68 H80 B4 F24 Fe N2 O2 P3	
Formula weight	1605.34	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 19.846(4) Å	α= 90°.
	b = 25.821(5) Å	β= 90°.
	c = 26.862(5) Å	γ = 90°.
Volume	13765(5) $Å^3$	
Z	8	
Density (calculated)	1.549 Mg/m^3	
Absorption coefficient	0.402 mm^{-1}	
F(000)	6600	
Crystal size	.25 x .15 x .15 mm^3	
Theta range for data collection	1.50 to 25.18°.	
Index ranges	-23<=h<=23, -30<=k<=30, -32<=l<=32	
Reflections collected	155016	
Independent reflections	12232 [R(int) = 0.0175]	
Completeness to theta = 25.18°	99.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12232 / 972 / 961	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0606, wR2 = 0.1680	
R indices (all data)	R1 = 0.0620, wR2 = 0.1692	
Largest diff. peak and hole	1.741 and -1.346 e.$Å^{-3}$	

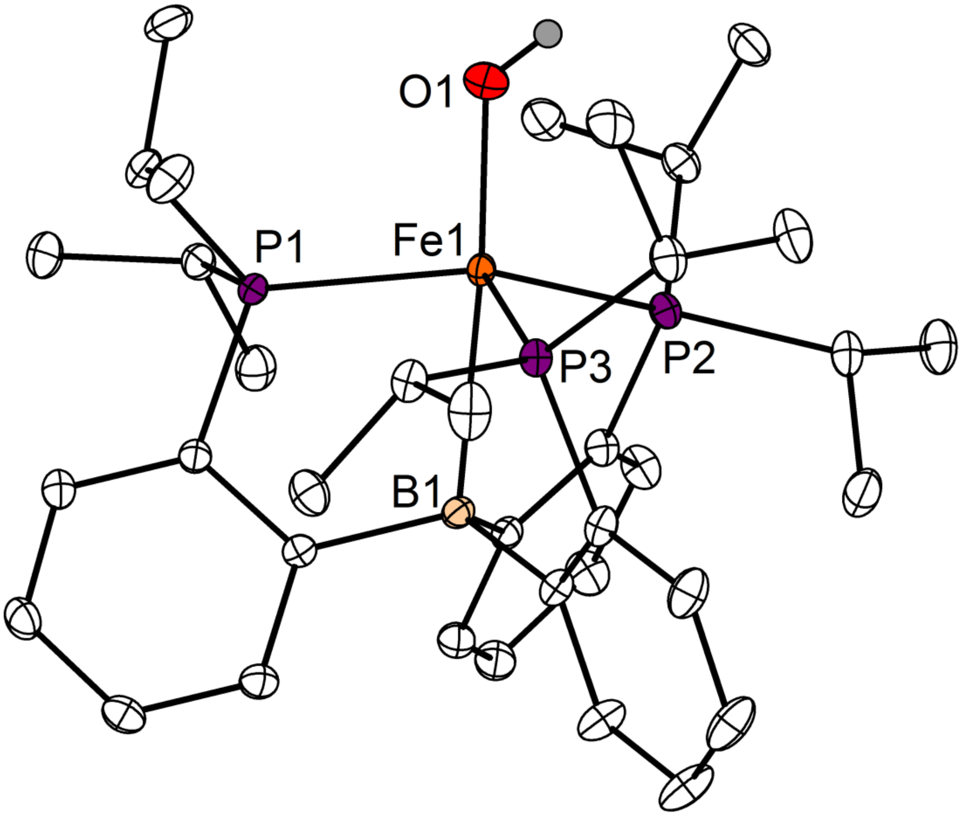
Table 6. Crystal data and structure refinement for (TPB)FeNH$_2$ (**5**)

Identification code	jsa23_0m	
Empirical formula	C36 H56 B Fe N P3	
Formula weight	662.39	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.9229(9) Å	α= 77.268(7)°.
	b = 11.2493(13) Å	β= 84.862(5)°.
	c = 16.5084(15) Å	γ = 61.117(4)°.
Volume	1732.1(3) Å^3	
Z	2	
Density (calculated)	1.483 Mg/m^3	
Absorption coefficient	0.615 mm^{-1}	
F(000)	812	
Crystal size	0.23 x 0.15 x 0.15 mm^3	
Theta range for data collection	2.11 to 28.28°.	
Index ranges	-14<=h<=14, -14<=k<=14, -22<=l<=22	
Reflections collected	52847	
Independent reflections	8561 [R(int) = 0.0706]	
Completeness to theta = 28.28°	99.7 %	
Max. and min. transmission	0.9134 and 0.8715	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8561 / 2 / 397	
Goodness-of-fit on F^2	1.120	
Final R indices [I>2sigma(I)]	R1 = 0.0545, wR2 = 0.1236	
R indices (all data)	R1 = 0.0810, wR2 = 0.1324	
Largest diff. peak and hole	1.541 and -0.646 e.Å^{-3}	

Table 7. Crystal data and structure refinement for (TPB)FeOH (**6**)

Identification code	jsa21_0m	
Empirical formula	C36 H56 B Fe N O P3	
Formula weight	678.39	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.9554(4) Å	α= 77.466(2)°.
	b = 11.3311(4) Å	β= 78.105(2)°.
	c = 16.6454(7) Å	γ = 61.338(2)°.
Volume	1757.30(12) $Å^3$	
Z	2	
Density (calculated)	1.282 Mg/m^3	
Absorption coefficient	0.595 mm^{-1}	
F(000)	726	
Crystal size	10.00 x 0.29 x 0.17 mm^3	
Theta range for data collection	2.07 to 37.78°.	
Index ranges	-18<=h<=17, -19<=k<=19, -28<=l<=28	
Reflections collected	142106	
Independent reflections	18846 [R(int) = 0.0433]	
Completeness to theta = 37.78°	100.0 %	
Max. and min. transmission	0.9056 and 0.0661	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	18846 / 1 / 382	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0316, wR2 = 0.0745	
R indices (all data)	R1 = 0.0477, wR2 = 0.0810	
Largest diff. peak and hole	0.810 and -0.493 e.$Å^{-3}$	

Figure 26. Crystal Structure for (TPB)FeOH (**6**)



Note that hydrogens have been omitted for clarity.